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(54) Composition for ink vehicles and protective coatings.

(57) An improved composition for use as a liquid vehicle in ink systems and for printing on diverse substrates. The functional constituents of the composition are unsaturated fatty acid esters, difunctional or multifunctional acrylate esters and optionally mixed esters of unsaturated fatty acid and difunctional or multifunctional acrylates and other alpha, beta unsaturated carboxylates. Lithographing ink vehicle formulations of these improved components exhibit exceptional performance. In application, the improved compositions permit a substantial reduction or elimination of solvents and certain drying agents that otherwise form toxic and environmentally sensitive byproducts.

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This invention relates to a specific class of compositions that exhibit a unique combination of physical properties consistent with exceptional inking characteristics. More particularly, the present invention relates to low or non-solvent ink vehicles for use in ink printing operations characterized by good wetting and adhesive properties.

BACKGROUND OF THE INVENTION

Printing technology has evolved over the centuries from a discipline considered an art form to one now dominated by the strictures of organic and surface chemistry. In the present context, inks are film forming compositions that dry to a thickness between 0.2 and 30 microns. In general, inks consist of two major components: the colorant (a pigment or dyestuff) and the vehicle (the liquid carrier that suspends or dissolves the colorant). The primary functions of the vehicle is to carry the colorant to the printed surface and thereafter harden and bind the colorant to the surface.

Although the technology underlying ink printing extends back several centuries, the industry supports a high profile, fast paced rate of technical advancement. The contours of the marketplace are continually placing new restrictions and pressures on ink developers. Recently, this is reflected by the advanced computer control presses capable of speeding the stock through the various printing stations at unprecedented rates. Although this permits substantial increases in printing output, it significantly reduces the attendant drying time. This translates to ink formulations having a requisite dry/cure period that corresponds to the faster cycles.

A related development involves worker and the general public's exposure to specific hazardous compounds in the plant environments and nearby community. Occupational Safety and Health Agency (OSHA) and Environmental Protection Agency (EPA) requirements regarding toxic and potentially carcinogenic materials have significantly restricted the permitted environmental concentrations of commercially important solvents. In response, the solvent loading and heavy metal drying agents in ink formulations must be handled in a manner that inhibits the build-up of solvents and/or other toxins in the plant, its environment and its waste streams.

It can be recognized that the above factors have created a strong incentive to printers to reduce and/or eliminate the solvents and heavy metal dryers employed in their ink formulations. The problem, of course, is that ink performance is usually tied directly to threshold levels of solvents that preserve low viscosity, spreadability, and good color (pigment) distribution. There has, heretofore, been a trade-off between speed and performance, and the above-noted environmental concerns.

Prior art ink systems have normally consisted of organic composition comprising oils and resins, appropriate viscosity controlling solvents, dryers and of course the requisite pigment or dyestuff. During the printing operation, the composition is selectively applied to the substrate and thereafter cured. Exemplary constituents include drying vegetable oils such as glyceride esters of unsaturated fatty acid esters. The unsaturation or double bond content of these esters permits a spontaneous crosslinking reaction in the presence of oxygen. For example, linolenic acid (the main constituent of linseed oil) and its isomeric varieties have long been effective drying components of coating and printing ink compositions. Attention is directed to The Printing Ink Manual, Van Nostrand Reinhold (Int'l) Co., Ltd. 4th Ed. (1988) which is herein incorporated by reference as if restated in full.

Oils have often been combined with selected resins such as (polydicycyclo) pentadiene, rosin, polyterpenes and alkyds to promote drying and film integrity over time. Both natural and synthetic resins have been used, but the major difficulty in application remains the matching of oil/resin properties that address a broad level of requirements. There continues to exist a market need for new and improved formulations of coatings and inks such that the liquid vehicles are substantially solvent-free and also suitable for simple, quick and low cost effective curing, without the need for additives, e.g., hazardous organic peroxides or radiation for radical formation or heavy metal ions as so-called driers, e.g., cobalt and manganese.

It was the above challenges that gave rise to the development of the present invention.

SUMMARY OF THE INVENTION

It is object of the present invention to provide new and improved low or nonsolvent ink vehicles prepared by combining difunctional and or oligofunctional unsaturated fatty acid esters with difunctional or multifunctional alpha, beta unsaturated carboxylate esters in a blend or in a unimolecular species that can be cured rapidly at ambient or elevated temperatures without resorting to hazardous exogenous catalysts.

It is another object of the present invention to provide a composition for ink vehicles that exhibits low viscosity with minimal or no solvent loading thereby avoiding high cost investment in plant equipment and labor for the scrubbing of hydrocarbon or distillate solvents.

It is a further object of the present invention to provide a fluid carrier at ambient temperature that is efficiently

applied to many diverse substrate materials.

It is yet another object of the present invention to provide a hardenable surface coating that is highly resistant to abrasion and corrosion.

It is a further object of the present invention to provide a method of preparing a low solvent or non-solvent ink system with superior curing properties.

It is still another object of the present invention to provide a method of printing using a vehicle comprising di and/or oligo unsaturated fatty acid esters in combination with difunctional or multifunctional alpha, beta unsaturated esters.

The above and other objects of the present invention are realized in a specific illustrative composition comprising a blend of di unsaturated and/or oligo unsaturated fatty acid esters in combination with difunctional or multifunctional alpha, beta unsaturated carboxylate esters at selected concentrations. The following compounds are suitably employed in the inventive compositions and at the designated proportions and

(i) a di and/or oligo unsaturated fatty acid ester component of general formula,

$$[C_nH_{2(n-x)+1}C(O)O\text{-}]_mR; \qquad (I)$$

(ii) a difunctional or multifunctional acrylate ester or derivative component of general formula,

$$[A(H)C{=}C(B)C(O)O\text{-}]_mR; \qquad (II)$$

wherein

R is a divalent or oligovalent hydrocarbyl or oxygenated hydrocarbyl radical having from two to eighteen carbon atoms;

A and B are independently hydrogen, monovalent hydrocarbyl ligands or oxygenated hydrocarbyl ligands with up to six carbon atoms each ligand;

n is an integer ranging from 6 through 21;

x is an integer ranging from 2 through 4;

m is an integer ranging from 2 through 11; and

the components (i) and (ii), collectively, being at least about 30% by weight and each component not less than about 10% by weight of the liquid portion.

In accordance with the varying aspects of the present invention, the bifurcated system expressed above can alternatively be formed as a combination (iii) representing the constituents of formulas (I) and (II) in a molecule. In this context, the inventive composition conforms to the following representation:

a mixed ester component combining both unsaturated fatty ester and alpha, beta di and/or oligo unsaturated carboxylate functions according to the general formula,

$$[C_nH_{2(n-x)+1}C(O)O\text{-}]_m[A(H)C{=}C(B)C(O)O\text{-}]_mR; \qquad (III)$$

wherein

R is a divalent or oligovalent hydrocarbyl or oxygenated hydrocarbyl radical having from two to eighteen carbon atoms;

A and B are independently hydrogen, monovalent hydrocarbyl ligands or oxygenated hydrocarbyl preferably carboxylate ligands of up to six carbon atoms each;

n is an integer ranging from 6 through 21;

x is an integer ranging from 2 through 4;

m is an integer ranging from 2 through 11; and

the component (iii) being at least about 25% by weight of the liquid portion.

DETAILED DESCRIPTION OF THE INVENTION

The preparation of the compositions according to the above delineated formulas is based on a combination of mixed esters of di and/or oligo unsaturated fatty acid and difunctional and/or multifunctional alpha, beta unsaturated carboxylic acid and derivatives thereof separately or as a hybrid molecular species to produce liquid vehicles which can carry pigments for implementation in an ink system.

The di and/or oligo unsaturated fatty acid esters are defined by the general formula

$$[C_nH_{2(n-x)+1}\ C(O)O\text{-}]_mR; \qquad (I)$$

the difunctional and/or multifunctional alpha, beta unsaturated carboxylate esters or derivatives thereof are defined by the general formula

$$[A(H)C{=}C(B)C(O)O\text{-}]_mR; \qquad (II)$$

and the di and/or oligo unsaturated fatty acid ester plus alpha, beta unsaturated carboxylate ester combined in a single molecular species are defined by the general formula

$$[C_nH_{2(n-x)+1}C(O)O\text{-}]_m[A(H)C{=}C(B)C(O)O\text{-}]_mR; \qquad (III)$$

wherein

R is a divalent or oligovalent hydrocarbyl or oxygenated hydrocarbyl radical having from two to eighteen

carbon atoms;

A and B are independently hydrogen, monovalent hydrocarbyl ligands or oxygenated hydrocarbyl ligands with up to six carbon atoms each;

n is an integer ranging from 6 through 21;

x is an integer ranging from 2 through 4; and

m is an integer ranging from 2 through 11.

The above relationships depict a selected range of molecular compounds that are related in functionality in the context of the systems employed for ink printing and coatings. The following Tables A-C provide a cross-section of suitable species satisfying the requirements of formulas (I), (II) and (III), respectively, consistent with the present invention.

TABLE A

A list of acceptable difunctional/oligofunctional unsaturated fatty esters useful in the practice of the instant invention:

a) ethylene glycol bis 6,8- undecadienoate
b) propylene glycol bis eleomarganate
c) pinol hydrate bis eleostearate
d) tripropylene glycol bis linoleate
e) pentaerythritol tris 7,11- behenadienoate
f) arabtol tetrakis 7, 9, 11- tridecatrienoate
g) linseed oil
h) tung (chinawood) oil
j) safflower oil
k) dehydrated castor oil

TABLE B

A list of acceptable difunctional or multifunctional alpha, beta unsaturated carboxylate esters useful in the practice of the instant invention:

a) trimethylolpropane trimethacrylate
b) trimethyolpropane triacrylate
c) glycerol acrylate, bis (methyl) maleate
d) bis oleyl fumarate
e) polybutadiene diacrylate
f) pentadecanediol dicrotonate
g) tetraethylene glycol bis angelate
h) mannitol pentaacrylate
j) 1,6 - hexanediol bis cinnamate
k) tris 2 - (2-methyl) propenolatoethyl trimelitate
l) methylene propane trimethacrylate

TABLE C

The following is a list of species containing both difunctional or oligo-functional unsaturated fatty acid ester and alpha, beta unsaturated carboxylate ester functionalities useful in the practice of the instant invention:

a) glycerol methacrylate, bis eleostearate,
b) bis linalool maleate,
c) pentaerythritol bis crotonate, bis linolate,
d) pinol hydrate acrylate, 9,11- tetradecadienoate,
e) trimethylol propane bis furoate, eleomargate,
f) ethylene glycol bis 2,4- undecadienoate,
g) 2-propenoatoethyl linolenate,
h) castor oil tris 2,4- undecadienoate,
j) 1,2,4 - hexanetriol - 1,2 - cyclomaleate - 2,4 - hexadecadienoate, and
k) propylene glycol (methyl) itaconate, 4,6-pentadecadienate.

As can be realized, the hybrid molecule expresses the functionality of the di and/or oligo unsaturated fatty acid ester and alpha, beta unsaturated carboxylate ester materials in a single molecule.

The concentrations of the compounds expressed by the above formulas determine the effectiveness of the resulting compositions. Obviously, the intended use of the composition will affect the relative balance therein. To meet non-solvent requirements, the ink vehicle will preferably comprise 30% or more of combined (I) and (II) and/or (III); in other systems with some level of permitted solvent, the combined weight percent of (I), (II) and (III) will always exceed 20%. In relative terms, compounds (I) and (II) will preferably be characterized by concentrations in weighted relation, with the understanding that the concentration for each will always exceed 10%.

In the alternate configuration involving the hybrid molecule, the concentration controls the resulting properties. Again, as with the above bifurcated system, solvent use should be minimized. Reasonable operating performance is obtainable with concentrations of formula (III) compounds exceeding 25% for ink liquid vehicles.

Moreover, it is understood by those skilled in the art that the important viscosity is the suitable working viscosity during the actual printing operation. Depending on the application, a wide variety of additives are operable to contour the system properties to the application. These additives include surfactants such as soaps, detergents and/or coupling agents; reactive diluents such as low molecular weight unsaturated esters, amides and/or urethanes (which otherwise act as solvating agents), monofunctional acrylates and derivatives thereof, and aziridines; slip agents such as polytetrafluoroethylene, paraffin wax, polyethylene; bodying agents such as polyacrylates, fumed silica and bentonite clays; and autoxidation catalysis (for ambient air cured systems) such as cobalt, cerium, manganese and zirconium.

The foregoing features of the present invention will be more readily apparent in the context of a specifically delineated set of examples directed to the application of the compositions to specific uses. Ten separate examples for the inventive inks are provided below as applied to the following specific uses and surfaces: ink offset paper coatings (Example 1), sheet-fed lithographic printing on offset paper (Example 2), web coldset printing on uncoated paper (Examples 3 and 9), hot web offset lithography or web heatset ink (Examples 4, 5 and 6), and sheet fed printing on plastic substrates (Examples 7 and 10).

These examples are comparative in nature, being shown side by side with conventional compositions to evaluate the performance. The various formulations are presented first, followed by a presentation of the resulting ink performance.

EXAMPLE 1

This example teaches the benefits of the instant invention with respect to emissions reduction, dry rate and rub resistance of ink coatings on offset paper as compared to the prior art. The results are listed in Table 1. In particular, it will be apparent in comparing the test samples with the controls that Example 1 demonstrates significant reduction in dry time and considerably enhanced the rub resistance for certain inventive formulations (T_2, T_3, T_5 and T_6) in addition to the virtual elimination of solvent emissions.

TABLE 1

Formulations (PBW)[1]

All formulations contained 13 parts of yellow pigment (AAA), 1 part of polytetrafluroethylene (Teflon), 3 parts of carnuba wax, and 0.5 parts of surfactant(a)[2] respectively. In addition the control formulations required the addition of 0.5 each of 6% cobalt and manganese driers in order to reduce dry times to tolerable levels.

Formulations	C_1	C_2	C_3	C_4	T_1	T_2	T_3	T_4	T_5	T_6	T_7
Phenolic modified rosin ester	35	35	20	21	21	21	21	21	21	21	21
Gelled soya oil[3]	13.5	10.5	28.5	32.5	32.5	32.5	32.5	32.5	32.5	32.5	32.5
520° Mineral spirits	32	25		-	32	-	-	-	-	-	-
No. 3 soya oil	-	-	-	-	-	-	-	-	-	5	10
No. 3 linseed oil		-	10	10	-	25	20	15	30	5	-
Castor oil tris acrylate	-	-	-	25	5	10	15	-	20	-	-
Glycerol methacylate bis eleostearate	-	-	-	-	-	-	-	-	-	25	10
Dry time (hr)	21	34	28	13	11	1.4	0.3	24	2.6	1.2	4.8
Tabor abrasion (100 cycles)	F	F	F	F	F	P	P	F	P	P	F

Notes: 1, parts by weight; 2, Zirconium IV bis (bis 2,2-pro-penolatomethyl) butanolato, cyclo bis (bis 2,2 propenolato - methyl) butanalato diphosphato 0,0; 3, partially hydrogenated (non-drying) oil.

EXAMPLE 2

The Example 2 demonstrates that the compositions according to the present invention (e, h, j, k) do not require heavy metal driers such as cobalt or manganese in pigmented ambient air-cured paper coatings. Formulations according to the invention and comparative controls were prepared by admixing the components as indicated below on a two roll-mill. The resultant products were applied to separate sheets of offset paper by means of conventional lithography using a standard solvent-free citric acid/guar gum based fountain solution.

Formulations of Example No. 2

Component (Wt%)	e	f[1]	g[2]	h	i	k
Lithol Rubine Pigment (LRP)	15	15	15	15	15	15
Bodied Tung Oil	25	-	-	-	25	-
No.3 Coconut Alkyd[3]	5	-	54	-	-	-
Naphthenic Oil[4]	-	-	25	-	-	-
Bisphenol A Diacrylate	25	50	-	-	-	-
Oligomer MW 3000	20	31	-	-	-	-
Acrylic Resin MW 12,000	4	-	-	5.5	-	-
T-Butyl Peroxy Benzoate	-	2	-	-	-	-
1,4-Butynediol	-	1	-	1	-	-
Surfactant b[5]	0.5	0.5	0.5	0.5	0.5	0.5
Tris 0,0',- methacrylato castor oil	-	-	-	35	-	84.5
Tris 0,0',0[2] methacrylato linseedonato-0, pentaerythritol	-	-	-	19	59.5	-

1,4-Dimethoxy-benzene	0.5	-	0.5	-	-	-
Co naphthenate 12%	-	0.5	0.5	-	-	-
Mn naphthenate 12%	-	-	0.5	-	-	-
Trimethylol Propane Tri Acrylate (TMPTA)	5	-	-	25	-	-

NOTES: (1) Formulation (f; control) would not dry within 48 hours without drier (Co);
(2) Formulation (g; control) would not dry within 48 hours without both driers (Mn and Co);
(3) non-drying vehicle
(4) BP (boiling point) 400-470 degrees F.;
(5) 1,4 - Butynediol.

The comparative results are listed in Table 2 below.

TABLE 2

Test Method	e	f	g	h	i	k
Drying Time (Hr.)	2.4	3.4	5.7	2.0	1.8	2.1
24 hr. Pencil Hardness	2H	3H	2H	3H	3H	3H
Solvent Resistance[1]	P	P	F	P	P	P
Abrasion Resistance[2]	P	P	P	P	P	P
Gloss (60 gardner)	52	34	50	57	55	51

NOTES: P=pass; F=fail;
(1) 200 methyl ethyl ketone rubs;
(2) 200 cycle Tabor abrasion test.

Example 2 demonstrates that in comparison the embodiment of the present invention (e) air-dries substantially faster than conventional competitors (f and g) without the need for toxic heavy metal accelerators, affords a superior high gloss product and exhibits satisfactory hardness as well as resistance to solvent and abrasion.

EXAMPLE NO. 3

The following example shows the utility of the instant formulations in the preferred embodiments of newspaper or the so-called web coldset inks. Comparative formulations were prepared by milling together the indicated combinations of different types of liquid vehicle, pigment, and additives. The preparations subsequently were applied to uncoated bond stock on a sheet-fed press employing the indicated fountain solution(s). Resulting products were tested for abrasion resistance, solvent resistance, gloss, and dot gain.

Formulations of Example No. 3				
Ingredients (parts by weight)	a	b	c	d (ctl)
Lithol Rubine Pigment (LRP)	6	6	7	8
Tris [6-(2-Methyl) propenoato]hexanoato tris 1,1,1 hydroxy methylpropane	-	47	-	-
Acrylated bodied castor oil	70	-	-	-
Methacrylated light castor oil	-	-	25	-
Heavy corn oil (No. 9)	-	-	-	16
Light china oil	19	-	36	-
Heavy china oil (HC; No. 9)	-	45	30	37
470 Naphtha solvent	-	-	-	34
Carnuba wax	3	-	-	3
Dinonyl Phenol Ethoxylate (DPE)	2	-	2	2
DPN	-	2	-	-

The formulations, 3a, 3b, 3c, and 3d, for comparison were mixed four times on a water-cooled mill to give solutions having a viscosity of (47 +/-3) x 10^3 centipoise measured at 2 rpm using a Brookfield HBT viscometer. The products (3a, 3b, 3c and 3d) were applied to uncoated sheet-fed stock using a Multilith single color press to simulate a newsprint environment and an agar/manganese nitrate based fountain solution.

Based on comparative observations of several copies, the preferred embodiments formulated according to the present invention dried faster than the control formulation (3d), produced essentially rub-free products compared to the easily rubbed and distorted control, and provided sharper dot structures. In fact, the dot gain of the instant embodiments was found to be less than 5%, as against approximately 22% of the control. Despite the substantial reductions in pigmentation in instant Examples (3a, 3b, and 3c) as compared to control (3d), the instant formulations provided more robustly colored prints which was possibly due to enhanced transfer properties of the preferred embodiments.

EXAMPLE NO. 4

The following example serves to illustrate the advantageous properties of the present invention for embodiments used in hot web offset lithography. The advantages observed in addition to the obvious elimination of volatile organic compound solvents (VOCS) included reduced drying energy requirements, enhanced image sharpness which was reflected in reduced dot gain, reduced ink requirements at comparable image intensities, and enhanced tack stability. Tack is an empirical quantity that reflects the degree of cohesion of a film surface. Tack is an important property of ink, particularly, in the case of high speed printing where the stickiness of ink strongly affects the sharpness of the printed image.

Black ink formulations were prepared by dispersing the indicated proportions of ingredients followed by filtration through 5 micron screening to remove residual oversized solid matter. Subsequently, each composition was run independently on a conventional hot web offset press at a preset speed of approximately 1,100 feet per minute at full coverage. Drying was accomplished in a 30 foot oven using a web temperature and chill roll combination at the lowest controlled temperature needed to effect commercially adequate dry properties required for product folding. Other properties were measured immediately (offline) for the dried product. The ink flow to rollers was adjusted to compensate for varying output and print color intensities during startup in each case.

Formulation of Example No. 4

Component (Parts By Weight)	a(Ctl)	b	c	d	e	f
HC	31	32	40	30	30	30
Heavy Corn Oil	8	8	-	5	5	5
Black Pigment (Carbon Black)	14	14	14	14	14	14
Toner (Alkali Blue)	2	2	2	2	2	2
Polyethylene Powder	3	3	3	3	3	3
Acrylic Resin Powder	-	4	4	4	4	6
2-Butyl Glycerol Triacrylate	-	35	35	-	20	40
Surfactant a[1]	0.5	0.5	0.5	0.5	0.5	0.5
Surfactant b[2]	0.5	0.5	0.5	0.5	0.5	0.5
520°F by Naphtha	40	-	-	-	-	-
Teflon Powder	1	1	1	1	1	1
Bisphenol A dimethacrylate	-	-	-	40	21	-

The results are presented in Table 4.

NOTES: (1) Surfactant a = Zirconium IV bis (bis 2,2 propenolatomethyl) butanolato, cyclo bis (bis 2,2 propenolato-methyl) butanolato disphosphato O,O;
(2) Surfactant b = 1,4 Butynediol.

TABLE 4

	a	b	c	d	e	f
Min Dry Temp. (deg. F)	390	355	340	370	355	340
60 Gloss	61	57	59	55	58	59
Rub	P	P	P	P	P	P
% Dot Gain	23	15	11	11	13	8
Apparent Sq. ft. coverage/lb	980	1320	1270	1405	1310	1390
P=pass; F=fail						

The data in Table 4 show that the formulations (4b-4f) of the instant invention dry at lower temperatures and provide significantly enhanced coverage per weight and reduced dot gain over the control (4a). Thus, the preferred embodiments (4b-4f) compare well in terms of a satisfactory rub and gloss with control formulation (4a). In addition to the improved energy efficiency, the VOCS of the instant formulation is reduced from

approximately 250 to 400 g/liter of ink to essentially nil.

EXAMPLE NO. 5

The following example is directed to compositions of web heatset inks in accordance with the combined general formulas (I) and (II) which are free of solvent (VOCS) and heavy metal driers or couplers (metal catalysts). The main difficulty in producing acceptable solid heat-set inks using a resinous vehicle is apparently due to the insufficiently uniform particulate size and dispersal of acrylic powder in the absence of solvents (VOCS) or distillates. Instead of pursuing the required extensive milling or grinding by various methods, a new blending process was introduced. Specifically, acrylic thermoplastic resin free of hydrocarbon or distillate solvents was melted into methacrylate ester or fatty acid ester thus effecting a vehicle for inks of uniform consistency and good shelf life. Moreover, it was found that the gloss and drying properties of the solvent-free inks could be enhanced by using solid acrylic resin compounds of both low (about 3,000) and medium (about 17,000) molecular weight in the liquid vehicle.

Accordingly, mixtures of resinous vehicle components were prepared in two separate batches: Batch A consisted of 70% gelled soya oil and 30% acrylic resin (Acryloid\ DM55, solid, Rohm and Haas). Batch B consisted of 90% trimethylene propane trimethacrylate (SR350; Sartomer Corporation) and 10% acrylic resin (Acryloid\ B66, solid, Rohm and Haas). Batch A was heated to about 180°C to a smooth semi-clear amber colored varnish and cooled to about 100°C. Batch B was heated to about 120°C, stirred and cooled to about 100°C, producing a low viscosity water-white vehicle. Finally, equal amounts of these batches were blended at about 100°C producing semi-clear amber-colored vehicle of a viscosity very similar to bodied china wood oil (range: 75,000-150,000 centipoise at rest). This liquid vehicle component was designated BDM 3500. Four ink formulations suitable for e.g., high gloss magazine stock are shown below as prepared in the colors yellow (a), magenta (b), cyan (c), and black (d). It is noted that the absence of heavy metal drying agents or coupling agents further avoids serious environmental hazards.

Components (% Parts by Weight)	(a)	(b)	(c)	(d)
Pigment MX yellow (sun)	13.0	-	-	-
Pigment Rubine (sun)	-	13.5	-	-
Pigment Phthalocyanine blue (sun)	-	-	13.5	-
Carbon black regal 400 R (cabot)	-	-	-	14.0
Alkali blue pigment (sun)	-	-	-	3.0
bodied China wood oil	20.0	25.0	25.0	20.0
SR350	15.0	20.0	20.0	18.0
BDM 3500	46.0	36.0	36.0	40.5
Polyethylene micro wax powder	2.7	1.7	1.7	1.7
Polytetrafluoroethylene (PTFE)	1.0	1.0	1.0	1.0
Silicone	2.0	2.5	2.5	2.6
Hydroquinone	.3	.3	.3	.3
Total (%)	100	100	100	100

The solvent-free ink formulations of Example 5 exhibited excellent printing properties, having only little dot gain acceptable water pickup, exceptional transfer, satisfactory gloss in the finished product, and needing less ink for matching the color density of conventional ink formulations. As shown in Table 5 below, although free of solvents and driers, all inks exhibited working characteristics ranging from acceptable to excellent. For example, the tack sequence as indicated allows the correct sequential deposition of the color inks, starting with

black followed by the colors with increasingly lighter hues and commensurately decreasing tack.

TABLE No 5

(Web Heatset Inks)				
Formulation	(a)	(b)	(c)	(d)
Water Pick-up	59	46	49	43
Tack Sequence	10.2	11.1	12.4	13.8
Gloss (% of control)	70	70	70	70

EXAMPLE NO. 6

The following example demonstrates the feasibility of using an environmentally acceptable "active oxygen" (hydrogen peroxide) source in conjunction with certain preferred formulations in order to obtain significant reductions in energy consumption and potentially enhanced speed of drying compared to a conventional ink.

This test was directed to heatset inks prepared according to the formulations No. 6 and printed on 100 lb. coated offset paper and 20 mil clear polyethylene terphthalate (Pet) stocks. Samples (6b) and (6c) represent the inventive system comparable to the control sample (6a). The results of these tests are given in Table 6.

Formulation #6: Heatset Inks			
Ingredient part (%)	a (Ctl)	b	c
Heavy linseed oil	28	28	20
Heavy corn oil	18	18	14
Phthalocyanine blue pigment	12	12	12
Teflon Powder	1	1	1
Polyethylene Powder	3	3	3
Surfactant (a)	1	1	1
470 degree mineral spirits	35	-	-
fumed silica	2	2	2
tetramethylol acetone tetramethacrylate	-	35	32
water	-	-	47

Formulated inks were each milled three times prior to application using a standard heatset web press as full coverage patterns at 10,000 impression/hr fountain solutions employed were solvent free guar gum-magnesium nitrate-water and independently guar gum-magnesium nitrate-3% hydrogen peroxide solution. Results are given in Table 6.

TABLE 6

Temp. Formulation (Fountain Solution)	Min. Dry Temp. (deg F) Coated Paper	Min Dry (deg F) Pet
Control Formulation #6a (water)	380	390
Control Formulation #6a (Peroxide)	370	370
Test Formulation #6b (Water)	340	350
Test Formulation #6b (Peroxide)	310	320
Test Formulation #6c (Water)	320	320
Test Formulation #6c (Peroxide)	310	320

EXAMPLE 7

A similar test is shown in the following Example 7, but now directed to sheet fed ink systems. Again, the control is a related composition of more conventional make-up, comparable to two separate embodiments of the present invention, test 1 and test 2, respectively.

Formulation #7: Sheet-fed Inks

Ingredient (Part By Weight)	Control	Test #1	Test #2
Heavy linseed oil	35	35	35
Heavy soya oil	9	15	15
Carnuba Wax	3	3	3
Phthalocyanine blue pigment	14	14	14
Teflon Powder	1	1	1
Surfactant a	1	1	1
520° mineral spirits	35	-	-
Fumed silica	2	-	-
Acrylated castor oil	-	29	-
TMPTM	-	-	15
PEM	-	-	14

Formulated inks were each milled three times prior to application on coated paper and PVC stocks using a standard single color (multilith) sheet-fed lithographic press using gum arabic-citric acid and gum arabic-citric acid-6% hydrogen peroxide fountain solutions. The minimum drying times are given in Table 7.

TABLE NO. 7

Formulation	Min Dry Time (min) Gum/Citrate/Water	Min Dry Time (Min) Gum Citrate/6%
Control Paper	55	57
Control PVC	>3600	>3600
Test #1/Paper	<3	<1
Test #1/PVC	60	12
Test #2/Paper	<3	<1
Test #2/PVC	35	8

The test compositions formulated according to the present invention clearly outperformed the control compositions with regard to rapid drying times both on paper and PVC surfaces (see Table No. 7), thereby demonstrating the advantageous properties of the instant heatset and sheet-fed ink formulations.

Our following embodiments have been found to provide an attractive blend of properties consistent with the needs of the particular industry:

EXAMPLE 8

I. Newsprint Ink

Formulation	Parts By Weight
Acrylated Castor oil	24
China wood oil	16
Black pigment	12
Alkali Blue Pigment	2
Heavy corn oil	10
Castor oil	24
Surfactant[1]	0.5
Polytetrafluoroethylene (PTFE)	1
Hydrated Lime	0.5
Soya Alkyd	10

Note: 1) Titanium IV 2-propanolato, tris (dioctyl) phenyl sulfonato-O.

EXAMPLE 9

Coldset Web Ink Formulation	Parts By Weight
Carbon Black Pigment	16
Alkali Blue pigment	3
Acrylated castor oil	15
China wood oil	20
Soya Alkyd[1]	4
Heavy corn oil	10
Surfactant[2]	0.5
Hydrated lime	0.5
PTFE	1.0

Notes: 1) Varchem, Clifton, N.J.;
2) Titanium IV 2-propanolato, tris (dioctyl) phenyl sulfanato-O

The total invention ingredients: 35 weight%.

EXAMPLE 10

Sheetfed Plastics/Nonporous Substrate Ink

Formulation	Parts By Weight
Trimethylopropane Triacrylate	15
Trimethylolpropane Trimethacrylate	28
Red pigment	15
Butyl Acrylate/Methyl Methacrylate Copolymer	5
Linseed Alkyd	16.5
Soya gel	10
Heavy corn oil	6
Surfactant[1]	0.5
Polyethylene	3
PTFE	1

Note: 1) Titanium IV (bis 2,2 - propenolatomethyl) butanolato (bis octyl) diphosphato-O adduct with 2 moles of N,N dimethyl amino propyl (2-methyl) propenoamide.

The above-described arrangement is merely illustrative of the principles of the present invention. Numerous

modifications and adaptations thereof will be readily apparent to those skilled in the art without departing from the spirit and scope of the present invention.

Claims

1. A liquid vehicle for use in ink formulations comprising combinations of (i) di and/or oligo unsaturated fatty acid ester and (ii) a difunctional or multi-functional alpha, beta unsaturated carboxylate ester.

2. The liquid vehicle of claim 1 wherein the combined components (i) and (ii) are at least 30% by weight, but each component not less than about 10% by weight of the total liquid vehicle.

3. An ink composition comprising the liquid vehicle of claim 1 in combination with a colorant.

4. The ink composition of claim 3 further comprising a drying agent.

5. The liquid vehicle of claim 1 wherein the components are defined as
(i) a di and/or oligo unsaturated fatty acid ester component of general formula,

$$[C_nH_{2(n-x)+1}C(O)O\text{-}]_mR; \qquad (I)$$

(ii) a di- or multi-functional alpha, beta unsaturated carboxylate ester or derivative component of general formula,

$$[A(H)C{=}C(B)C(O)\text{-}]_mR; \qquad (II)$$

wherein R is a divalent or oligovalent hydrocarbyl or oxygenated hydrcarbyl radical having from two to eighteen carbon atoms; A and B are independently hydrogen, monovalent hydrocarbyl ligands or oxygenated hydrocarbyl ligands with up to six carbon atoms each ligand;
n is an integer ranging from 6 through 21;
x is an integer ranging from 2 through 4; and
m is an integer ranging from 2 through 11.

6. An ink composition comprising the liquid vehicle of claim 1, wherein component (i) is selected from a group consisting of: China wood Oil and Methyl Linoleate, and component (ii) is selected from a group consisting of: Trimethylol propane trimethacrylate (TMPTM) and Phenoxyethyl Methacrylate (PEM).

7. A printed article including print symbols comprising a cured portion of the liquid vehicle of claim 3 on a substrate.

8. A liquid vehicle for use in ink formulation comprising a mixed ester component combining in a molecule di and/or oligo unsaturated fatty acid and optionally derivatized di or multifunctional alpha, beta carboxylate functions.

9. The liquid vehicle of claim 8 wherein the mixed ester component (iii) is defined by the general formula,

$$[C_nH_{2(n-x)+1}C(O)O\text{-}]_m[A(H)C{=}C(B)C(O)O\text{-}]_mR, \qquad (III)$$

wherein
R is a divalent or oligovalent hydrocarbyl or oxygenated hydrocarbyl radical having from two to eighteen carbon atoms;
A and B are independently hydrogen, monovalent hydrocarbyl ligands or oxygenated hydrocarbyl ligands of up to six carbon atoms each;
n is an integer ranging from 6 through 21;
x is an integer ranging from 2 through 4; and
m is an integer ranging from 2 through 11.

10. The liquid vehicle of claim 8 wherein the mixed ester component is at least 25% by weight of the liquid vehicle.

11. An ink composition comprising the liquid vehicle of claim 8 in combination with a colorant.

12. The ink composition of claim 11 further comprising a drying agent.

13. An ink formulation comprising the liquid vehicle of claim 9, wherein component (iii) is selected from a group consisting of: trimethylol propane diacrylate linolenate, pentaerythritol trimethylate delta 9-myristate and

tri (9-propenato-O)-delta-11-octadecenateo-), propane (1,2,3) triol.

14. A liquid vehicle for coating or ink formulation comprising
(i) a di and/or oligo unsaturated fatty acid ester component,
(ii) a difunctional or multi-functional alpha, beta unsaturated carboxylate ester component or derivative thereof, and
(iii) a mixed ester component containing both di and/or oligo unsaturated fatty acid and di or multi-functional alpha, beta unsaturated carboxylate functions or derivative thereof.

15. An ink formulation comprising the liquid vehicle of claim 14 containing at least about 25% by weight of a combination of components (i) and (ii) and at least about 5% by weight of component (iii).

16. An ink formulation consisting essentially of the liquid vehicle of claim 14.

17. The liquid vehicle of claim 1 wherein the di and/or oligo unsaturated fatty acid ester is selected from the group consisting of:
Ethylene glycol bis 6,8- undecadienoate,
propylene glycol bis eleomarganate,
pinol hydrate bis eleostearate,
tripropylene glycol bis linoleate,
pentaerythritol tris 7,11- behenadienoate,
arabitol tetrakis 7, 9, 11- tridecatienoate,
linseed oil,
tung (China wood) oil,
safflower oil,
soya oil,
dehydrated castor oil,
and the difunctional and/or multi-functional alpha, beta unsaturated carboxylate esters selected from a group consisting of:
Trimethylolpropane trimethacrylate,
trimethylolpropane triacrylate,
glycerol acrylate, bis (methyl) maleate,
bis oleyl fumarate,
polybutadiene diacrylate,
pentadecanediol dicrotonate,
tetraethylene glycol bis angelate,
mannitol pentaacrylate,
1,6 hexanediol bis cinnamate,
tris 2-(2-methyl) propenolatoethyl trimelitate.

18. The heavy metal drier-free lithographic ink composition comprising the liquid vehicle of claim 1, a pigment, a surfactant, and a solid resin.

19. The liquid vehicle of claim 14 wherein the components are defined as
(i) a di and/or oligo unsaturated fatty acid ester component of general formula,

$$[C_nH_{2(n-x)+1}C(O)O\text{-}]_mR; \qquad (I)$$

(ii) a di- or multi-functional alpha, beta unsaturated carboxylate ester or derivative component of general formula,

$$[A(H)C{=}C(B)C(O)\text{-}]_mR; \text{ and} \qquad (II)$$

(iii) a mixed ester component containing both di and/or oligo unsaturated fatty acid and alpha, beta unsaturated di-functional or multi-functional carboxylate ester functions or derivative thereof according to the general formula,

$$[C_nH_{2(n-x)+1}C(O)O\text{-}]_m[A(H)C{=}C(B)C(O)O\text{-}]_mR; \qquad (III)$$

wherein
R is a divalent or oligovalent hydrocarbyl or oxygenated hydrocarbyl radical having from two to eighteen carbon atoms;
A and B are independently hydrogen, monovalent hydrocarbyl ligands or oxygenated hydrocarbyl ligands of up to six carbon atoms each;
n is an integer ranging from 6 through 21;

x is an integer ranging from 2 through 4; and
m is an integer ranging from 2 through 11.

20. A method of printing comprising the steps of:
a. preparing a printing ink comprising the liquid vehicle of claims 1, 8 or 14, with a colorant; and
b. applying said printing ink on a substrate material.

21. The liquid vehicle of claim 8 wherein the mixed ester component is selected from a group consisting of:
glyceryl methacrylate, bis eleostearate,
bis linalool maleate,
pentaerythritol bis crotonate, bis linolate,
pinol hydrate acrylate, 9,11- tetradecadienoate,
trimethylol propane bis furoate, eleomargate,
ethylene glycol bis 2,4- undecadienoate,
2-propenoatoethyl linolenate,
castor oil tris 2,4- undecadienoate,
1,2,4 - hexanetriol cyclomaleate, 2,4 - hexadecadienoate, and
propylene glycol (methyl) itaconate, 4,6-pentadecadienate.

22. An ink formulation for web heatset printing comprising the liquid vehicle of claim 1 which is devoid of solvents and drying or coupling metal catalysts and which comprises at least about 20% by weight, preferably about 30% by weight, each of trimethylene propane methacrylate ester and the unsaturated fatty acid ester selected from the group consisting of China wood oil and soya oil.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 2031

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-3 804 640 (G.R. BUCKWALTER) * Claims * ---	1	C 09 D 11/02 C 09 D 11/06
A	US-A-4 147 674 (J.A. VASTA) * Abstract; column 6, example 1 * ---	1	
X	DATABASE WPIL, accession no. 90-073064 [10], Derwent Publications Ltd, London, GB; & JP-A-02 028 273 (TORAY IND. INC.) 30-01-1990 * Whole abstract * -----	1,18	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C 09 D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	15-06-1992	CATURLA VICENTE V.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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(54) **Vegetable oil based thermosetting lithographic ink system**

(57) Rapid thermosetting, low VOC web offset lithographic inks are prepared in the instant invention from solid resin, drying oil alkyds, bodied drying oil, vegetable oil, fatty acids, multifunctional unsaturated polyester, reducing agents and transition metal salts of organic acids. The aqueous lithographic fountain solution contains hydroperoxides or peroxides which promote free radical polymerization of the ink in contact therewith. The metal salts of organic acids function as crosslinking agents in combination with excess carboxylic acid functionality of the ink. Optionally, the reducing agent and the organic hydroperoxide or peroxide may be interchanged.

EP 0 731 150 A1

Description

This invention relates to novel, low volatile organic component (VOC) lithographic printing ink systems and methods for ink film production using the novel systems. The invention particularly relates to rapidly heat curable lithographic ink systems containing catalytic redox means and cross-linking agents for the combined initiation of free radical polymerization and crosslinking of vegetable oil based printing inks containing unsaturated polyester resin(s) having available carboxylic acid groups. The ink film produced by the invention is virtually 100% solids and tack-free.

The volatile organic component (VOC) as a percentage of printing inks is rapidly becoming an important environmental issue. Formulations in many ink types have traditionally consisted of relatively high molecular weight polymers, a mixture of additives, pigment, and one or more volatile hydrocarbon solvents. These solvents may represent a potential worker exposure hazard and are also known to contribute to the tropospheric air pollution problem as well.

In order to overcome the problems associated with using solvents, both in the ink industry and other coatings industries, new technologically advanced products have arrived on the market. Present technology includes the use of water borne, high solids, and powder coating systems. High solids products are based on the solventless system in which polymerization occurs after application of the coating or ink are also available. These products usually employ relatively low molecular weight, highly functional resins in conjunction with a cross-linking agent and a "reactive diluent", if necessary, for viscosity reduction.

Lithographic printing is a process which utilizes a coated metal or polymeric plate containing a hydrophobic image area which accepts, i.e., it is wetted by, hydrophobic based ink and a non-image hydrophilic area which accepts water, i. e., the fountain solution. As practiced in the prior art, high speed web presses use inks that contain organic solvents to transport the ink. The drying of the printed ink film is achieved by solvent volatilization at a substrate temperature of about 150° - 200°C. Consequently, the use of such inks in the prior art requires highly sophisticated emission control equipment in order to comply with clean air and occupational standards for exposure to organic solvents. Considering these environmental standards and the costs associated with complying with them under practical industrial conditions, artisans in the field of ink development have been vigorously engaged in the development of new inks that will more readily meet environmental standards but still provide the quality performance demanded for the final printed product.

It is an objective of the present invention to provide a solvent-free, high solids, low VOC printing ink.

Another objective of the invention is to provide a solvent-free printing ink having a high level of flow properties, self structure capability and that is very fast drying.

Yet another objective of the invention is to provide the printing industry a solvent-free, fast drying, vegetable oil based "environmentally friendly" printing ink.

The foregoing objectives plus other features and advantages are achieved through the practice of the discoveries of the instant invention as described hereinafter.

Heat-set, low VOC web offset lithographic inks are prepared in the instant invention from solid resin, drying oil alkyds, bodied drying oil, vegetable oil, fatty acids, multifunctional unsaturated polyester, reducing agents and transition metal salts of organic acids. The lithographic fountain solution contains water soluble or emulsifiable hydroperoxides which promote free radical polymerization of the ink system when placed in contact with the ink formulation of the invention.

The invention provides a solvent-free lithographic printing ink that dries rapidly under the influence of heat. The invention is based on redox initiation systems composed of initiators such as free radical forming organic hydroperoxide and peroxide dissolved in a fountain solution and reducing agents such as ferrous compounds in the printing ink. Optionally, the hydroperoxide may be contained in the ink and the reducing agent contained in the fountain solution. The printing ink also contains organometallic compounds, i.e., zirconium carboxylates that function as crosslinking agents. Upon application of heat during heat set drying, thermal curing takes place via free radical crosslinking between unsaturated materials and crosslinking reaction through interaction between carboxy groups contained in the printing vehicles and organic acid salts where the organic acid has an acid functionality of at least 2. Zirconium compounds of organic acids are preferred.

More particularly, the invention is a vegetable oil-based, heat curable lithographic printing ink system comprising a first part comprising a liquid lithographic printing ink containing pigment, a vegetable oil based rosin ester, unsaturated polyester resin(s) having free carboxylic acid groups, a reducing agent and a cross-linking agent comprising an organometallic salt; and a second part comprising an aqueous fountain solution containing an organic hydroperoxide or peroxide. The reducing agent may be contained in the fountain solution while said organic hydroperoxide or peroxide is contained in said ink.

In a preferred embodiment, the aqueous fountain solution contains between 1-5 weight percent of organic hydroperoxides or peroxides as an oxidizing agent. The liquid lithographic printing ink contains between 1-10 weight percent of a reducing agent, 1-5 weight percent of a cross-linking agent comprising an organometallic salt, 5-60 weight percent of vegetable oil based rosin ester, 5-30 weight percent pigment and 5-20 weight percent unsaturated polyester resin(s) having free carboxylic acid groups.

The present invention employs a two part thermosetting ink system for curing or drying vegetable oil based lithographic printing ink on non-metallic plate or film. The first part contains pigment, vegetable oil based rosin ester gel, one or more reducing agents, a polyester formed by esterification of an aliphatic polyol and C_{12} to C_{20} unsaturated fatty acid, an aromatic polyester modified with trimellitic anhydride to produce a resin containing free carboxylic acid groups, and organometallic salts having a functionality of at least 1. Preferably, zirconium compounds are included as the organometallic salt which are capable of forming strong crosslinking bonds with the free carboxylic acid groups of the foregoing resins.

The second part consists of an aqueous lithographic fountain solution containing free radical forming and water miscible hydroperoxides, peroxides, or both.

The present invention is derived from the discovery that when the novel lithographic ink system described above as parts 1 and 2 is substituted for a conventional ink system as used in lithographic printing plate preparation, i.e., ink and fountain solution, the free radical initiating catalysts contained in the aqueous fountain solution and normally used to treat the hydrophilic part of the lithographic plate migrates into or is absorbed in the liquid ink deposited on the oleophilic image part of the plate when these two components inevitably come into contact during dampening in the plate making process. When the catalyst in the fountain solution is absorbed into the liquid ink on the imaging surface, a composition is thereby formed that lends itself to redox initiated, free radical polymerization and crosslinking of olefinic unsaturation in the ink vehicle upon heating. Further, it has been discovered, the presence of excess carboxylic acid functionality in the liquid ink and organometallic salts produces additional crosslink formation when the system is subjected to heat or thermosetting treatment.

The phenomenon of catalyst migration from fountain solution into ink vehicle, it has been discovered, is not restricted to the migration of organic hydroperoxide or peroxide migration from fountain solution into the ink vehicle. For example, the reducing agent contained in first part, the ink vehicle, as taught above may optionally be contained in the second part, the fountain solution, while the organic hydroperoxide or peroxide is added to the ink vehicle formulation. The process of the invention proceeds as well in either configuration.

Ferrous compounds are preferred in the invention as reducing agents to form free radicals by redox reaction with hydroperoxide during drying process. Particularly preferred ferrous compounds are ferrous ammonium sulfate, ferrous sulfate, ferrous lactate, ferrous naphthenate and ferrous oxalate. However, other lower valence state salts can be used as reducing agents.

Free radical forming oxidizing agents useful in the compositions of the invention include cumene hydroperoxide, benzoyl peroxide and tertiary butyl hydroperoxide.

Printing ink compositions based on the vehicles and additives of the invention may employ a wide variety of pigments. Examples of suitable pigments are: phthalo cyanine blue, benzidine yellow, litho rubine red, and carbon black.

The ink system of the invention can be dried or cured at temperatures between 100°C and 180°C, preferably between 150 - 180°C.

While not intending to be constrained by theoretical consideration, it is believed that the process of the invention involves the following curing mechanisms when the treated printed plate is dried between 150 - 180°C:

Oxidation-reduction reaction between hydroperoxide and ferrous compounds produces the free radicals which propagate the polymerization or drying of vegetable oils producing crosslinks with multi function unsaturation present in the ink system;

zirconium compounds react strongly with carboxylic acid groups, forming covalent bonds while hydrogen bonds are formed with hydroxy groups which, in combination, further enhances the drying of the novel printing ink of the invention.

Since no volatile reaction by-products are produced by the process of the invention, the product of the invention is essentially 100% non-volatile. The novel printing ink is stable for long periods since there are no driers and/or free radical forming hydroperoxides or peroxides present in the ink system when the ink system is formulated to include reducing agents. The use of zirconium compounds as crosslinking agents, ferrous compound as reducing agent and hydroperoxide and peroxide in the fountain solution, significantly lowers the drying time of the printed ink without disturbing the stability of the ink system.

In the following Examples all four colors, including cyan blue, magenta red, yellow and black printing inks were trialed on a 2/color 25" G.P.I. Miehle Press at 6,000 sheets/1 hour, impression. A Westvaco sterling litho gloss paper was used as a printing substrate. All four colors were printed at standard web offset printing optical density ranging from 1.01 to 1.75. After printing, these sheets were tested for drying on a sinvatrol drying tester with a belt speed of 40 ft./min. at 150 to 180°C temperature. A total of 1000 sheets were printed for each color.

The two part printing ink system of the invention depicted in the following examples consists of printing ink compositions using ferrous compound as reducing agent in the first part. The second part consists of a concentrate Roso KSP #500 M-3 fountain solution diluted with tap water according to the manufacturer's instructions. To the diluted fountain

solution water miscible tertiary butyl hydroperoxide-70 was added as free radical forming to provide a 5% solution of oxidizing solution.

A high solid, low VOC soya oil based heatset printing ink having the following composition was prepared. The first three examples illustrate the application of ferrous compound as reducing agent in the fountain solution and free radical forming oxidizing agent in the ink formulation. All inks were prepared by first preparing a concentrated base material, consisting pigment, varnish and reactive diluent. This base was then used to prepare the final ink formulation. The ink formulas are described in the following by parts and percentage by weight.

Example 1

Ink Formulation	Parts
1. Soya oil based rosin ester	56.00
2. Phthalo blue pigment	15.00
3. Conjugated linoleic acid	9.00
4. Unsaturated cycloaliphatic oligomer (Astrocure - 78)	10.00
5. Polyethylene wax	5.00
6. t-butyl hydroperoxide	5.00
	100.00

Prior to the printing process 5% ferrous sulfate was added to diluted Roso KSP #500 M-3 fountain solution. When the printing process takes place, the ink comes in contact with ferrous sulfate via fountain solution. An oxidation - reduction reaction between t-butyl hydroperoxide of the ink and ferrous sulfate of the fountain solution forms the free radicals which propagate the crosslinking reaction between the unsaturated materials of the ink. As a result the ink is dry to the touch at 150 to 180°C within 1 second.

Example 2

Example 1 was repeated by substituting tertiary butyl hydroperoxide with cumene hydroperoxide. The resultant ink, in the presence of ferrous sulfate in the fountain solution, is dry to the touch at 150 - 180°C temperature within 1 second.

Comparative Example

Example 2 was repeated without using ferrous sulfate reducing agent in the fountain solution. The resultant ink does not dry to the touch at 150°C within 1 second. The results indicted that a reducing agent, for example ferrous sulfate, is required to form free radicals by redox reaction which helps to dry the ink by free radical crosslinking reaction at a lower temperature of 150°C.

Example 3

Examples 3 to 7 illustrate the application of ferrous compound as a reducing agent in the ink formulation and oxidizing agent, for example t-butyl hydroperoxide - 70 in the fountain solution. It also describes the second drying mechanism by crosslinking carboxy groups containing polyester and zirconium compounds to obtain through dry to the print at higher optical density between 1.60 to 1.90. Following is the ink formulation:

Ink Formulation	Parts
1. Soya oil based rosin ester	43.52
2. Phthalo blue pigment	14.25
3. Linseed oil based polyester	4.75
4. Carboxy group containing polyester	14.25
5. Conjugated Linoleic acid	9.95
6. Ferrous Naphthenate	5.70
7. Zirconium Propionate	1.88
8. Polyethylene/PTFE wax	4.75
9. Zinc Neodeconate	0.95
	100.00
Fountain solution: Roso KSP #M-3 + 5% t-butyl hydroperoxide-70. The ink, when printed on a 38 inch Miehle sheetfed press, showed no signs of offset and dried to the touch within 1 second at 150° - 180°C.	

Example 4

This heatset ink was prepared by substituting ferrous naphthenate with cerium octoate. The material oxidizes the hydroperoxide to form free radicals, which crosslink the unsaturation material of the ink during the ink drying process. The following is the ink formulation:

Ink Formulation	Parts
1. Soya oil based rosin ester	44.90
2. Phthalo blue pigment	19.25
3. Carboxy group containing polyester	2.55
4. Conjugated linoleic acid	6.40
5. Linseed oil based polyester	6.40
6. Cerium Octoate	8.98
7. Polyethylene/P-T-F-E Wax	8.97
8. Zirconium Propionate	2.55
	100.00

Example 5

High solid, low VOC , magenta red heatset ink was prepared by utilizing the following formulation:

Ink Formulation	Parts
1. Soya oil based rosin ester	44.90
2. Litho rubine red pigment	19.65
3. Linseed oil based polyester	6.50
4. Conjugated linoleic acid	7.55
5. Carboxy group containing polyester	5.70
6. Polyethylene/P-T-F-E wax	6.85
7. Zirconium Propionate	3.15
8. Ferrous Naphthenate	5.70
	100.00

The resultant ink was dry to the touch at 150°C within 1 second.

Example 6

Transparent yellow heatset ink was prepared by the following formulation:

Ink Formulation	Parts
1. Soya oil based rosin ester	41.70
2. Transparent yellow pigment	10.65
3. Linseed oil based polyester	3.55
4. T.M.A. modified benzoate ester	14.90
5. Conjugated linoleic acid	18.05
6. Ferrous Naphthenate	4.65
7. Polyethylene/P-T-F-E wax	3.70
8. Zirconium Propionate	2.80
	100.00

The resultant ink of Example 6 dried at 150°C within 1 second.

Example 7

High solids black heatset ink was prepared as follows:

Ink Formulation	Parts
1. Soya oil based rosin ester	32.85
2. Carbon black pigment	11.45
3. Linseed oil based alkyd resin	3.80
4. Conjugated linoleic acid and T-M-A modified benzoate ester	20.00
5. Conjugated linoleic acid	19.90
6. Ferrous Naphthenate	5.00
7. Polyethylene/P-T-F-E wax	4.00
8. Zirconium Propionate	3.00
	100.00

The resultant inks of Examples 3 to 7 were dried by the dual mechanism: (1) free radical cross-linking reaction between unsaturated materials of the ink and (2) cross-linking reaction through interaction between carboxyl groups of the printing ink vehicle and zirconium compounds. The final print showed no signs of offset and dried to the touch at 150°C within 1 second.

Claims

1. A vegetable oil-based, heat curable lithographic printing ink system comprising:

   a first part comprising a liquid lithographic printing ink containing pigment, a vegetable oil based rosin ester, unsaturated polyester resin(s) having free carboxylic acid groups, a reducing agent and a cross-linking agent comprising an organometallic salt; and
   a second part comprising an aqueous fountain solution containing an organic hydroperoxide or peroxide.

2. The system of claim 1 wherein said reducing agent is contained in said fountain solution while said organic hydroperoxide or peroxide is contained in said ink.

3. The system of claim 1 or 2 wherein said rosin ester comprises soya oil based rosin ester.

4. The system of any of claims 1 to 3 wherein said polyester comprises the polymeric residue of an aliphatic alcohol, C_{12}-C_{20} unsaturated fatty acid and aromatic carboxylic acid(s) including at least one aromatic carboxylic acid having a functionality greater than 2.

5. The system of claim 4 wherein said unsaturated fatty acid comprises linoleic acid and said carboxylic acid(s) comprise a mixture of benzoic acid and trimellitic anhydride.

6. The system of any of claims 1 to 5 wherein said cross-linking agent is selected from carboxylic acid salts of Groups IIA-VIIIA transition metals of the Periodic Table of the Elements plus copper, aluminum, tin and lead.

7. The system of claim 6 wherein said cross-linking agent comprises zirconium propionate.

8. The system of any of claims 1 to 7 wherein said hydroperoxide or peroxide is selected from cumene hydroperoxide, benzoyl peroxide and tertiary butyl hydroperoxide.

9. The system of any of claims 1 to 8 wherein said reducing agent is selected from ferrous ammonium sulfate, ferrous sulfate, ferrous lactate, ferrous oxalate and ferrous naphthenate.

10. An organic solvent free, heat curable lithographic printing ink system comprising:

an aqueous fountain solution containing between 1-10 weight percent of a reducing agent; and
liquid lithographic printing ink containing 1-5 weight percent of a cross-linking agent comprising an organometallic salt, 1-5 weight percent of organic hydroperoxide or peroxide, 5-60 weight percent of vegetable oil based rosin ester, 5-30 weight percent pigment and 5-20 weight percent unsaturated polyester resin(s) having free carboxylic acid groups.

11. The system of claim 10 wherein said reducing agent is contained in said liquid lithographic printing ink while said organic hydroperoxide or peroxide is contained in said fountain solution.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 10 3423

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 79-55487B[30] XP002006084 & JP-A-54 076 304 (TOKYO INK KK) , 18 June 1979 * abstract * ---	1	C09D11/02
A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 93-252978[32] XP002006085 & JP-A-05 171 089 (SAKATA INKS CO. LTD.) , 9 July 1993 * abstract * -----	1	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)
C09D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19 June 1996	Niaounakis, M

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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